

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 March 2001 (29.03.2001)

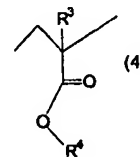
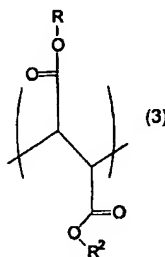
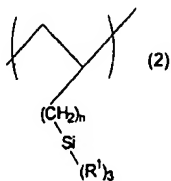
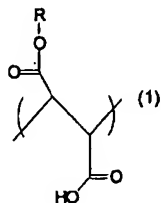
PCT

(10) International Publication Number
WO 01/22162 A2

- (51) International Patent Classification⁷: **G03F** **SLATER, Sidney, George**; 20 Teakwood Drive, Cumberland, RI 02864 (US). **STEINHAUSLER, Thomas**; Apt. 4, 365 Almond Willow Cove, Collierville, TN 38017 (US).
- (21) International Application Number: **PCT/US00/22141**
- (22) International Filing Date: **11 August 2000 (11.08.2000)** (74) **Agent: GREELEY, Paul, D.**; Ohlandt, Greeley, Ruggiero & Perle, L.L.P., 9th Floor, One Landmark Square, Stamford, CT 06901-2682 (US).
- (25) Filing Language: **English**
- (26) Publication Language: **English** (81) **Designated States (national)**: JP, KR, SG.
- (30) **Priority Data**: (84) **Designated States (regional)**: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- 09/401,111 22 September 1999 (22.09.1999) US
09/576,146 22 May 2000 (22.05.2000) US
- (71) **Applicant: ARCH SPECIALTY CHEMICALS, INC.** **Published:**
[US/US]; 501 Merrit 7, P.O. Box 4500, Norwalk, CT 06856-4500 (US). — *Without international search report and to be republished upon receipt of that report.*

- (72) **Inventors: FOSTER, Patrick**; 48 North Court Street, Providence, RI 02903 (US). **BIAFORE, John, Joseph**; 207 Lexington Avenue, Providence, RI 02903 (US). *For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) **Title: RADIATION SENSITIVE COPOLYMERS, PHOTORESIST COMPOSITIONS THEREOF AND DEEP UV BILAYER SYSTEMS THEREOF**



WO 01/22162 A2

(57) **Abstract:** Radiation sensitive resins for use as a top layer resist in a bilayer system for use in deep UV photolithography comprises derivatized copolymers having structural units (1), (2), (3) and (4) wherein n is 1 to 5, R is an alkyl group, R¹ a methyl or trimethylsiloxy, R³ is hydrogen or methyl and R² and R⁴ are each tert-butyl groups.

RADIATION SENSITIVE COPOLYMERS, PHOTORESIST COMPOSITIONS THEREOF AND DEEP UV BILAYER SYSTEMS THEREOF

Field of the Invention

This invention relates to new radiation sensitive copolymers for use as a top layer resist in a bilayer system for use in deep UV photolithography, particularly for 248 and 193 nm photolithography, and especially for 193 nm photolithography. The invention also relates to radiation sensitive photoresist compositions comprising the new copolymers and to a process for the lithographic imaging treatment of a substrate by means of the photoresist composition, as will a process for the production of electronic components using the new copolymers in a radiation sensitive photoresist top layer coating in a 248 or 193 nm lithographic system.

Background of the Invention

In recent years, the extent of integration of semiconductor components has been continually increasing. The resolution capacity that can be obtained with conventional deep-UV microlithography has thus appeared to reach its limits. Normally, it is not generally possible to produce, on a substrate, conventional structures with dimensions of less than 0.25 μm , as is required for the production of particularly highly integrated electronics components. These components generally have minimal dimensions down to approximately 0.12 μm . In order to be able to resolve sufficiently, in an optical manner, such fine structural elements, particularly short-wave radiation must be utilized, which generally has a wavelength between 190 and 260 nm.

However, present conventional G-line, I-line and deep-UV (DUV) photoresistant materials are poorly suited for radiation of such wavelength. These conventional materials are usually based on phenolic resins as binders, for example, on novolak resins or on chemically amplified polyhydroxystyrene derivatives with acid labile groups, which show a strong absorption at wavelengths below 260 nm. This leads to the

fact that, with the use of such radiation, the side walls of the finished developed resist structures do not form the targeted right angle, but rather form a more or less oblique angle with the substrate or the resist surface, which nullifies the obtaining of optical resolution as a consequence of the use of shortwave radiation.

Photoresists without a sufficiently high proportion of aromatic components, e.g., resists based on methacrylate resins, have proven sufficiently transparent for radiation below 260 nm, but they do not have the plasma etch resistance that is customary for resists based on aromatic resins; plasma etching being one principal method for producing microstructures on silicon substrates. The plasma etch resistance, as is known, is essentially based on the aromatic groups in these resists.

ArF excimer base (193 nm) lithography is a prime candidate for sub 0.18 μm lithography. The leading resist technology approaches for practical 193 nm lithography are top surface imaging (TSI) bilayer resists and single layer. Each approach has its own characteristic advantages and disadvantages as the result of the underlying technology and the materials, which can be utilized. The numerous problems for the 193 nm photoresist chemists to solve, (e.g., transparency, photospeed, adhesion, sensitivity, various process time delay latitudes, and plasma etch resistance), are somewhat different for each technology due to the materials requirements.

Lithographic aspect ratios and other issues require that resist films be thinner (about 0.5 μm) for sub 0.18 μm devices. This, in turn, requires either greatly improved etch processes or improved etch resistance or both. Thus, having excellent plasma etch resistance is critical and it is preferable that it be even better than before because of the thinner films. This presents a materials problem to the resist chemist because now both the aromatic character and the alkali-solubilizing group must be replaced. Thus, new materials, or groups of materials, with high transparency, etch resistance, and a different alkali-solubilizing group are required.

Single layer resists based on alicyclic polymers, for example, based on cyclic hydrocarbons such as norborene, have been found to be

transparent enough at 193 nm and to have reasonable plasma etch resistance. However, the alicyclic resins in their "pure state" suffer from high hydrophobicity and adhesion problems. Modifications to improve these and other properties tend to decrease the plasma etch resistance significantly below that of novolac based resins and offer little hope of improved etch resistance.

There have been various solutions proposed for this problem. One solution is offered by the use of a special multilayer technique, generally referred to as bilayer resists. First, an initial resin coating, commonly called an undercoat layer, which is not photoimageable, is introduced onto the substrate. This undercoat layer provides the plasma etch resistance when etching the substrate. A second covering coating layer that can be photoimaged, which contains an organosilicon component instead of a component with a high content of aromatic compounds, is introduced onto the first planarizing layer. The substrate coated in this way is selectively exposed, i.e., in an image-forming way, in the conventional manner and then treated with a suitable developer, so that a desired image-forming structure is generated in the covering coating that can be photostructured. A subsequently conducted treatment in oxygen plasma leads to the organosilicon compounds being oxidized to silicon oxides, at least on the surface, and these oxides form a closed etching barrier or protective surface over the unexposed areas, for the oxidative decomposition of the organic material that lies underneath, particularly the planarizing layer, while the planarizing layer is removed completely in an oxidative manner on those places that are not coated by the silicon-containing covering layer.

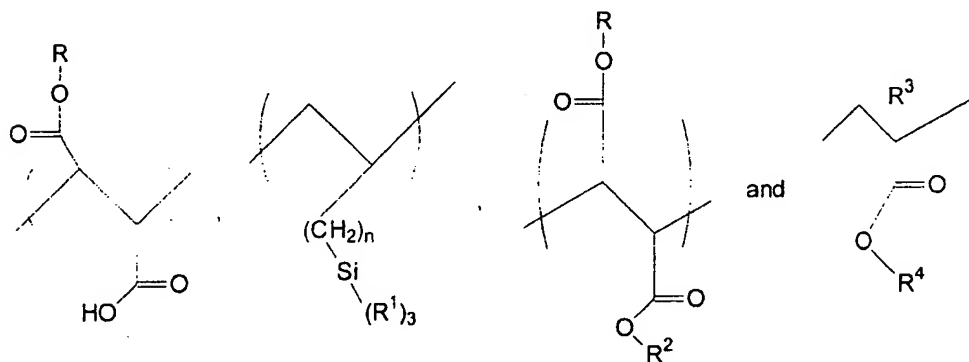
Such bilayer resists generally offer improved depth of focus, resolution, substrate compatibility, and aspect ratios.

While various polymers have been proposed for use in such photoimageable top layer compositions in a bilayer system for photolithography at 193 nm wavelength radiation there is still a need for improved polymers with improved lithographic properties for this purpose,

and especially for a bilayer system to provide high resolution deep UV lithography, particularly at 193 nm radiation.

Brief Summary of the Invention

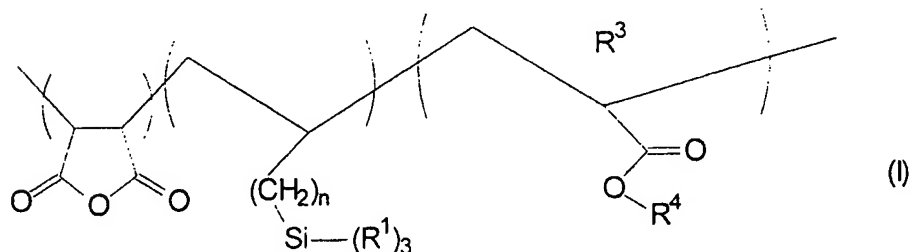
- 5 The present invention provides a novel copolymer derivative suitable for forming a top layer photoimageable coating in a deep UV, particularly a 193 nm, bilayer resist system providing high-resolution photolithography. The present invention also provides a new photoresist composition for forming a photoimageable coating on a substrate for use in
- 10 193 nm photolithography. The invention also provides a copolymer with chemically amplified (acid labile) moieties and organosilicon moieties suitable for use in the binder resin for photoimageable etching resistant photoresist compositions suitable for use in 248 and 193 nm photolithographic processes.
- 15 The novel derivatized copolymers of this invention have the following structural units:



- 20 wherein n is an integer of from 1 to 5, R is the alkyl residue of alkanol, preferably a C₁-C₄ alkyl group, especially a CH₃ group; R¹ is methyl or trimethylsiloxy; R³ is hydrogen or methyl and R² and R⁴ are tert-butyl radicals. It is preferred that n is equal to 1.

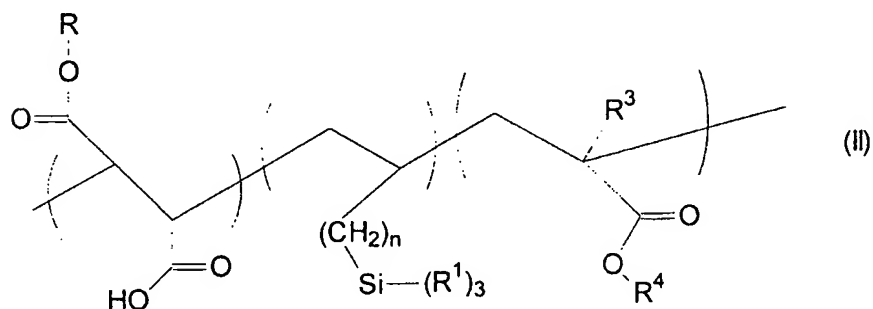
The novel derivatized copolymers of this invention are prepared by reacting maleic anhydride, an alkenyltrimethylsilane or alkenyl(tristrimethoxysiloxy) silane and t-butyl acrylate or methacrylate in a free radical polymerization reaction to form polymer (I) of the formula:

5



subjecting polymer (I) to partial alcoholysis of the maleic anhydride portion of the polymer by reaction with excess alkyl alcohol, preferably methanol, to produce polymer (II) of the formula:

10



and then derivatizing the carboxylic acid moiety of polymer (II) with dimethylformamide di-t-butylacetal to produce the derivatized copolymers of this invention.

15

Polymer (I) comprises about 40 to about 50 mole % maleic anhydride units, about 40 to about 50 mole % alkenyltrimethylsilane or alkenyl(tristrimethoxysiloxy) silane units, and up to about 20 mole % t-butyl methacrylate or acrylate units. The preferred molecular weight (Mw) of

polymer (I) is about 10,000 to about 40,000, preferably from about 15,000 to about 25,000.

Polymer (I) is subjected to partial alcoholysis by reaction with excess alkyl alcohols, such as for example, methanol, ethanol, propanol, butanol or other alkyl alcohols. The degree of alcoholysis (i.e., maleic acid ring opening) is determined by both temperature and reaction time of the alcoholysis, according to procedures known in the art.

The resulting polymer (II) contains a ring opened maleic anhydride monoalkylester with the degree of ring opening being up to 100% depending on the reaction conditions, preferably the degree of ring opening is between about 80 to about 100% of the maleic anhydride present in the polymer backbone of polymer (I).

The reaction of polymer (II) with dimethylformamide di-t-butylacetal converts some degree of the free carboxylic acid moiety of polymer (III) to a t-butyl ester to provide the novel derivatized copolymers of this invention. The degree of t-butyl ester derivatization depends on the amount of dimethylformamide-di-t-butylacetal present in the reaction, the reaction temperature and time, and the reaction solvent. The degree of t-butyl ester derivatization can range up to about 53% of the free carboxylic acid present in polymer (II), and is preferably a level of derivatization of from about 20 to about 35%.

The level of silicon in the derivatized copolymer of this invention will generally be at a level of from about 6 to about 14% by weight, preferably from about 8 to about 12% by weight which is sufficient to allow adequate pattern transfer into the undercoat of the bilayer resist system.

In addition to the units of the derivatized copolymers of this invention as described hereinbefore, other acrylate or methacrylate units, such as for example, methyl methacrylate or hydroxyethyl(meth)acrylate units, may be incorporated in a known manner into the derivatized polymer to enhance certain lithographic properties of the derivatized copolymer.

The derivatized copolymers of this invention are formulated in suitable solvents with photoacid generating (PAG) compounds which

generate acid upon exposure to radiation to provide photosensitive photoresist compositions useful in deep UV, particularly 193 nm, photolithography.

A bilayer coated substrate for use in deep UV

- 5 photolithography is produced by applying a suitable undercoat or planarizing layer to the substrate and then applying onto the undercoated substrate a photoimageable top layer of the photoresist composition of the derivatized copolymer described in the previous paragraph. The new derivatized copolymers of this invention provide photoresist compositions
- 10 suitable for use at 193 and 248 nm wavelength that produce an excellent combination of adhesion, resolution and plasma etch resistance.

Detailed Description of the Invention and Preferred Embodiments

- Preferred derivatized copolymers of this invention are those
- 15 wherein n is 1, R is CH_3 , R^1 is CH_3 , and R^3 is hydrogen and the degree of t -butyl derivatization of the free carboxylic acid of polymer (II) is from about 30 to about 38%.

- In formulating radiation sensitive photoresist compositions suitable for use as photoimageable top layers in deep UV bilayer
- 20 photolithographic systems, the derivatized copolymers of this invention are formulated with any suitable photoacid generator in a suitable solvent. The photoresist compositions of this invention will generally contain from about 80 to 99% by weight of the derivatized copolymer of this invention, and from about 1 to about 10% by weight photoacid generator. Other additives,
- 25 such as surfactants, bases pigments, dyes, colorants, filters, antistriation agents, bonding agents, leveling agents, wetting agents and softeners, may also be added to improve lithographic performance. These other additives can comprise from 0 to about 10% by weight of the composition. The photosensitive compositions, after formulation and coating onto a suitable
- 30 undercoated substrate, can then be imagewise patterned by exposure to actinic radiation from various sources of monochromatic light, such as for example, ArF excimer laser, KrF excimer laser and the like.

Any suitable photoacid generator, particularly onium sulfonate salts, which generate acid under the effects of active radiation from exposure sources ranging from electron beam, ArF excimer lasers and KrF excimer lasers can be used to form the radiation-sensitive compositions with the copolymers of this invention to prepare the radiation-sensitive photoresist compositions of this invention.

Among the suitable onium sulfonate salts, there may be mentioned particularly aryl sulfonium and iodonium sulfonates, especially triaryl sulfonium and iodonium sulfonates. The aryl groups of the sulfonium or iodonium moieties may be substituted or unsubstituted aryl groups, such as unsubstituted phenyl or naphthyl, or these moieties may be substituted by one or more substituents such as halogen, C₁₋₄ alkyl, C₁₋₄ alkoxy, -OH and/or nitro substituents. The aryl groups or substituents on each aryl group may be the same or different.

The anion of the photoacid generator may be any suitable anion of a suitable organic sulfonic acid, such as acids of aliphatic, cycloaliphatic, carbocyclic-aromatic, heterocyclic-aromatic or arylaliphatic sulfonic acids. These anions may be substituted or unsubstituted. Partially fluorinated or perfluorinated sulfonic acid derivatives or sulfonic acid derivatives substituted in the neighboring position to the respective acid group are preferred. Examples of substituents are halogens, such as chlorine, and particularly fluorine, alkyl, such as methyl, ethyl or n-propyl, or alkoxy, such as methoxy, ethoxy or n-propoxy and the like.

Preferably the anion is a monovalent anion from a partially fluorinated or perfluorinated sulfonic acid. Preferred are fluorinated alkyl sulfonate anions.

Special examples of suitable onium salts are triphenyl sulfonium bromide, triphenyl sulfonium chloride, triphenyl sulfonium iodide, triphenylsulfonium methane sulfonate, triphenylsulfonium trifluoromethane sulfonate, triphenylsulfonium hexafluoro-propane sulfonate, triphenylsulfonium nonafluorobutane sulfonate, triphenylsulfonium phenyl sulfonate, triphenylsulfonium 4-methylphenyl sulfonate, triphenylsulfonium 4-methoxyphenyl sulfonate, triphenylsulfonium 4-chlorophenyl sulfonate,

triphenyl-sulfonium camphorsulfonate, 4-methylphenyl-diphenylsulfonium trifluoromethane sulfonate, bis(4-methylphenyl)-phenylsulfonium trifluoromethane sulfonate, tris-4-methylphenylsulfonium trifluoromethane sulfonate, 4-tert-butylphenyl-diphenylsulfonium trifluoromethane sulfonate, 5 4-methoxyphenyl-diphenylsulfonium trifluoromethane sulfonate, mesityl-diphenylsulfonium trifluoromethane sulfonate, 4-chlorophenyldiphenyl-sulfonium trifluoromethane sulfonate, bis-(4-chlorophenyl)-phenylsulfonium trifluoro-methane sulfonate, tris-(4-chlorophenyl) sulfonium trifluoromethane sulfonate, 4-methyl-phenyl-diphenylsulfonium hexafluoropropane sulfonate, 10 bis(4-methylphenyl)-phenyl-sulfonium hexafluoropropane sulfonate, tris-4-methylphenylsulfonium hexafluoro-propane sulfonate, 4-tert-butylphenyl-diphenylsulfonium hexafluoropropane sulfonate, 4-methoxyphenyl-diphenylsulfonium hexafluoropropane sulfonate, mesityl-diphenyl-sulfonium hexafluoropropane sulfonate, mesityl-diphenylsulfonium nonafluorobutane 15 sulfonate, mesityl-diphenylsulfonium perfluorooctane sulfonate, 4-chlorophenyl-diphenylsulfonium hexafluoropropane sulfonate, bis-(4-chlorophenyl)-phenylsulfonium hexafluoropropane sulfonate, tris-(4-chlorophenyl) sulfonium hexafluoropropane sulfonate, diphenyliodonium trifluoromethane sulfonate, diphenyliodonium hexafluoro-propane 20 sulfonate, diphenyliodonium 4-methylphenyl sulfonate, bis-(4-tert-butylphenyl) iodonium trifluoromethane sulfonate, bis-(4-tert-butylphenyl)iodonium hexafluoro-propane sulfonate, bis-(4-cyclohexylphenyl)iodonium trifluoromethane sulfonate, tris(4-tert-butylphenyl)sulfonium perfluorooctane sulfonate, and bis-(4- 25 cyclohexylphenyl) iodonium hexafluoropropane sulfonate. Particularly preferred is triphenyl sulfonium trifluoromethane sulfonate (triphenyl sulfonium triflate).

If a base is employed in the photoresist composition, the base may be any suitable base compound, such as oxydianiline, piperonylamine, 30 hexamethyl-triethylenetetramine, 2,4,5-triphenylimidazole, 1,5-diazabicyclo[4,3,0]non-5-ane, or 1,8-diazabicyclo[5,4,0]undec-7-ane, preferably 2,4,5-triphenylimidazole.

Although any suitable solvent may be employed in

formulating the photoresist compositions of this invention, the solvent is preferably propylene glycol methyl ether acetate (PGMEA).

Another aspect of this invention is a process for the lithographic treatment of a substrate by means of a multilayer technique, in

5 which:

the substrate is provided with a first coating of a film-forming aromatic polymer material and then suitably cured,

a second coating containing a derivatized copolymer of the invention and a substance that forms acid under the effect of actinic radiation of a wavelength of about 193 nm, is introduced on this first coating,

the thus-coated substrate is irradiated in an image-forming way with radiation of a wavelength of 248 to 254 or of 193 nm, to which the photoacid generator is sensitive,

15 the irradiated substrate is subjected to a heat treatment,

the heat treated irradiated substrate is treated with an aqueous alkaline developer solution, until the irradiated regions of the second coating are removed, and

20 after this, the substrate is treated with an oxygen-containing plasma until the first coating is completely removed on those places where it is not covered by the second coating.

Any suitable film-forming organic polymers can be used as the film-forming organic material for the first coating (undercoat layer) with the use of the multilayer technique, such as phenolic resins, particularly 25 novolak resins, such as formaldehyde cresol or formaldehyde phenol novolaks, polyimide resins, poly(meth) acrylate resins, styrene-allyl alcohol copolymer resins, and preferably copolymers of isobornyl methacrylate and hydroxystyrene thermally cured or crosslined with hexamethoxy melamine as described in of US Patent Application No. 09/268,430 filed March 12, 30 1999. The undercoat layer is generally 0.5 to 1 μm thick. The undercoat resin is first dissolved in a suitable solvent and then introduced by the usual coating processes onto the substrate, e.g., by dipping, blade coating,

painting, spraying, particularly by electrostatic spraying, and reverse-roller coating, and above all by spinning, and subsequently cured by methods known in the art.

After the first layer is dried and cured, the second coating,
5 containing a derivatized copolymer of this invention, a substance that forms acid under the effect of actinic radiation of a wavelength below 300 nm, preferably below 260 nm, and more preferably at about 193 nm, as well as other additives, if needed, is introduced onto the first coating. The second coating may also be produced with any conventional coating process, for
10 example, one of those named above, but here also spin coating is particularly preferred. The covering layer is appropriately approximately 0.2 to 0.5 μm thick.

For the production of relief structures, the thin-s-coated substrate is then selectively exposed, i.e., to form the image. Exposure is
15 preferably produced with actinic radiation of a wavelength of 190-300 nm, particularly of 190 to 260 nm. A known source of the respective radiation can be utilized in principle for irradiation, for example, mercury high-pressure lamps, but particularly excimer lasers, such as the krypton fluoride (KrF) laser with radiation of 248 nm wavelength or the argon fluoride (ArF)
20 excimer laser with 193 nm radiation. The image-forming irradiation is produced either by means of a mask, preferably a chromium-quartz mask, or--when laser exposure devices are used--also by moving the laser beam in a computer-controlled manner over the surface of the coated substrate and thus the image is produced. Here, the high sensitivity of the
25 photoresist materials of the invention is very advantageous, especially noticeable in that it permits high writing speeds at relatively low intensities. The high sensitivity of the resist is also of advantage for exposure by means of steppers, where very short exposure times are desired.

The process of the invention also encompasses, between
30 selective irradiation and treatment with a developer, a heating of the coating as a further process measure. By means of this heat treatment, the so-called "post-exposure bake", a practically complete reaction of the resist material, is obtained in an especially rapid time. The time and temperature

of this post-exposure bake may vary within broad regions and essentially depend on the composition of the resist, particularly by the type of its acid-sensitive photoacid generator used, as well as the concentrations of these two components. Commonly, the exposed resist is subjected to several
5 seconds up to several minutes of temperatures of approximately 50-150°C.

After the image-forming exposure and heat treatment of the material conducted as needed, the irradiation areas of the top coat that are more soluble in aqueous alkaline as a consequence of the irradiation are dissolved out with an aqueous-alkaline developer, i.e., with an aqueous
10 solution of bases to which small quantities of organic solvents or their mixtures may also be added as needed.

Particularly preferred as developers are aqueous alkaline solution, as they are also utilized for the development of conventional novolak naphthoquinone diazide positive resist coatings. These include,
15 e.g., aqueous solutions of alkali metal silicates, phosphates, hydroxides, and carbonates, but particularly tetraalkylammonium hydroxide solutions, such as e.g., tetramethylammonium hydroxide solution, which is free of metal ions. Still smaller quantities of wetting agents and/or organic solvents may also be added to these solutions. Typical organic solvents,
20 which may be added to the developer fluids, are, for example, 2-ethoxyethanol, isopropanol or ethanol, as well as mixtures of two or more of these solvents.

After this, the thus-treated workpiece is treated with an oxygen or oxygen-containing plasma, whereby a closed silicon oxide layer
25 is formed within several seconds, at least in the uppermost regions of the top coating of organosilicon components in the covering layer, and this silicon oxide layer protects the regions of the organic material lying underneath against an attack of oxygen plasma. Treatment with the oxygen plasma is continued until the substrate is completely free in those
30 places where the top coating has been removed beforehand by means of the developer. In general, an etching time of 1 to 15 minutes is sufficient for this purpose.

The substrate can finally be subjected to a conventional

structuring treatment, e.g., a dry etching in halogen or fluorocarbon plasmas on those places free of the coating. After this, the entire protective coating is removed from the substrate, e.g., by dissolving with a suitable stripper or by O₂ plasma ashing, after which the depicted process cycle is repeated, if needed, in order to produce further structures on the substrate. Therefore, a process for the production of an object, particularly an electronic component, comprising the above-depicted process for the lithographic treatment of a substrate forms another embodiment of the invention.

10 The present invention is further illustrated by the following Examples. All parts and percentages are by weight and all temperatures are degrees Celsius unless explicitly stated otherwise.

Examples of Synthetic Procedures

15 **Example 1: Synthesis of Poly(maleic anhydride-allyltrimethylsilane-t-butyl-methacrylate)**

In a 250 ml, round bottom flask equipped with a reflux condenser and a gas inlet was combined maleic anhydride (11.09 g, 0.113 mol) and tetrahydrofuran (30 ml). The mixture was stirred under a N₂ atmosphere until all the maleic anhydride was dissolved. To this solution was added allyltrimethylsilane (12.91 g, 0.113 mol), t-butyl methacrylate (6.0 g, 0.042 mol) and 2,2'-azobisisobutyronitrile (0.186 g, 0.001 mol). The mixture was heated to 64°C, and the mixture was stirred at this temperature for 18 h. The reaction mixture was cooled to room temperature and added dropwise to hexanes (500 ml). The precipitate was filtered, and the solid was dried in vacuo (12 mm Hg) at room temperature for 1 h. The solid was dissolved in tetrahydrofuran (50 ml), and the solution was added dropwise to hexanes (500 ml). The precipitate was filtered, and the solid was dried in vacuo (0.2 mm Hg) at room temperature for 16 h giving poly(maleic anhydride-allyltrimethylsilane-t-butylmethacrylate) (20.5 g, 68.2%) as a white powder. ¹H NMR (d₆-acetone, 250 MHz): 35.8 mol % maleic anhydride, 39.6 mol % allyl-trimethylsilane, 24.6 mol % 5-butyl methacrylate. GPC (Waters Corp. liquid chromatograph[refractive index

detection, Millenium GPC V software, Phenogel-10, 7.8x250 mm column: 10-4A; 500A&50A, THF eluent}): $M_w=20,250$; Polydispersity=2.34.

Example 2: Alcoholysis of poly(maleic anhydride-allyltrimethylsilane-t-butyl-methacrylate)

In a 250 ml, round bottom flask equipped with a reflux condenser and a gas inlet was combined poly(maleic anhydride-allyltrimethylsilane-t-butylmethacrylate) (47.39 g) and methanol (200 ml). The mixture was heated to 64°C under a nitrogen atmosphere, and the mixture was stirred at this temperature for 20 h. The solution was cooled to room temperature and added dropwise to water (500 ml). The precipitate was filtered, and the solid was dried in vacuo (0.2 mm Hg) at room temperature for 16 h giving poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate) (50.51 g, 95.0%) as a white powder. GPC (Waters Corp. liquid chromatograph[refractive index detection, Millenium GPC V software, Phenogel-10, 7.8x250 mm column: 10-4A, 500A & 50 A, THF eluent]): $M_w=21,300$; Polydispersity=3.08. ^1H NMR (d_6 -acetone, 250 MHz): 39.5 mole % monomethyl maleic acid, 35.8 mole % allyltrimethylsilane, 24.7 mole % t-butyl methacrylate.

20

Example 3: t-Butyl derivatized poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate)

In a 250 ml, round bottom flask equipped with a reflux condenser and gas inlet was combined poly(monomethyl maleic acid-allyltrimethylsilane-t-butyl-methacrylate) (15.0 g, 0.057 moles monomethyl maleic acid) and toluene (60 ml). The mixture was heated to 80°C under a nitrogen atmosphere which resulted in a slurry of the polymer in toluene. To this mixture was added dimethylformamide di-t-butylacetal (14.84 g, 0.073 mol), and the mixture was stirred at this temperature for 5 h. The reaction mixture was cooled to room temperature and added dropwise to hexanes (500 ml). The precipitate was filtered, and the solid was dried in vacuo (0.2 mm Hg) at 50°C for 24 h giving the t-butyl blocked

25

30

poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate)
(14.37 g) as a yellow powder. ^1H NMR (d_6 -acetone, 250 MHz): 30% of free
carboxylic acid derivatized to 5-butyl ester. DSC (Perkin-Elmer thermal
gravimetric analyzer [TGA-7]): $T_g=143^\circ\text{C}$. GPC (Waters Corp. liquid
5 chromatograph [refractive index detection, Millenium GPC V software,
Phenogel-10, 7.8x250 mm column: 10-4A, 500A & 50A, THF eluent]):
Mw=23, 500; Polydispersity 2.86.

**Example 4: t-Butyl derivatized poly(monomethyl maleic acid-
10 allyltrimethylsilane-t-butylmethacrylate)**

In a 250 ml, round bottom flask equipped with a reflux
condenser and gas inlet was combined poly(monomethyl maleic acid-
allyltrimethylsilane-t-butyl-methacrylate) (15.0 g, 0.057 moles monomethyl
maleic acid) and toluene (60 ml). The mixture was heated to 80°C under a
15 nitrogen atmosphere which resulted in a slurry of the polymer in toluene.
To this mixture was added dimethylformamide di-t-butylacetal (14.84 g,
0.057 mol), and the mixture was stirred at this temperature for 5 h. The
reaction mixture was cooled to room temperature and added dropwise to
hexanes (500 ml). The precipitate was filtered, and the solid was dried in
20 vacuo (0.2 mm Hg) at 50°C for 24 h giving the t-butyl blocked
poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate)
(14.20 g) as a yellow powder. ^1H NMR (d_6 -acetone, 250 MHz): 22.9% of
free carboxylic acid derivatized to t-butyl ester. DSC (Perkin-Elmer thermal
gravimetric analyzer [TGA-7]): $T_g=143^\circ\text{C}$. GPC (Waters Corp. liquid
25 chromatograph [refractive index detection, Millenium GPC V software,
Phenogel-10, 7.8x250 mm column: 10-4A, 500A & 50A, THF eluent]):
Mw=21,400; Polydispersity 2.76.

**Example 5: t-Butyl derivatized poly(monomethyl maleic acid-
30 allyltrimethylsilane-t-butylmethacrylate)**

In a 250 ml, round bottom flask equipped with a reflux
condenser and gas inlet was combined poly(monomethyl maleic acid-
allyltrimethylsilane-t-butyl-methacrylate) (15.0 g, 0.046 moles monomethyl

maleic acid) and toluene (60 ml). The mixture was heated to 80°C under a nitrogen atmosphere which resulted in a slurry of the polymer in toluene. To this mixture was added dimethylformamide di-t-butylacetal (14.84 g, 0.023 mol), and the mixture was stirred at this temperature for 5 h. The reaction mixture was cooled to room temperature and added dropwise to hexanes (500 ml). The precipitate was filtered, and the solid was dried in vacuo (0.2 mm Hg) at 50°C for 24 h giving the t-butyl blocked poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate) (13.39 g) as a yellow powder. ¹H NMR (d₆-acetone, 250 MHz): 7.0% of free carboxylic acid derivatized to t-butyl ester. DSC (Perkin-Elmer thermal gravimetric analyzer [TGA-7]): T_g=145°C. GPC (Waters Corp. liquid chromatograph [refractive index detection, Millenium GPC V software, Phenogel-10, 7.8x250 mm column: 10-4A, 500A & 50A, THF eluent]): Mw=20, 800; Polydispersity 2.56.

15

Example 6: t-Butyl derivatized poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate)

In a 250 ml, round bottom flask equipped with a reflux condenser and gas inlet was combined poly(monomethyl maleic acid-allyltrimethylsilane-t-butyl-methacrylate) (15.0 g, 0.046 moles monomethyl maleic acid) and toluene (60 ml). The mixture was heated to 80°C under a nitrogen atmosphere which resulted in a slurry of the polymer in toluene. To this mixture was added dimethylformamide di-t-butylacetal (14.84 g, 0.069 mol), and the mixture was stirred at this temperature for 5 h. The reaction mixture was cooled to room temperature and added dropwise to hexanes (500 ml). The precipitate was filtered, and the solid was dried in vacuo (0.2 mm Hg) at 50°C for 24 h giving the t-butyl blocked poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate) (13.67 g) as a yellow powder. ¹H NMR (d₆-acetone, 250 MHz): 38.3% of free carboxylic acid derivatized to t-butyl ester. DSC (Perkin-Elmer thermal gravimetric analyzer [TGA-7]): T_g=138°C. GPC (Waters Corp. liquid chromatograph [refractive index detection, Millenium GPC V software, Phenogel-10, 7.8x250 mm column: 10-4A, 500A & 50A, THF eluent]):

Mw=22, 580; Polydispersity 2.66.

Example 7: t-Butyl derivatized poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate)

- 5 In a 250 ml, round bottom flask equipped with a reflux condenser and gas inlet was combined poly(monomethyl maleic acid-allyltrimethylsilane-t-butyl-methacrylate) (15.0 g, 0.057 moles monomethyl maleic acid) and toluene (60 ml). The mixture was heated to 80°C under a nitrogen atmosphere which resulted in a slurry of the polymer in toluene.
- 10 To this mixture was added dimethylformamide di-t-butylacetal (14.84 g, 0.106 mol), and the mixture was stirred at this temperature for 5 h. The reaction mixture was cooled to room temperature and added dropwise to hexanes (500 ml). The precipitate was filtered, and the solid was dried in vacuo (0.2 mm Hg) at 50°C for 24 h giving the t-butyl blocked
- 15 poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate) (13.97 g) as a yellow powder. ¹H NMR (δ-acetone, 250 MHz): 52.4% of free carboxylic acid derivatized to t-butyl ester. DSC (Perkin-Elmer thermal gravimetric analyzer [TGA-7]): T_g=141°C. GPC (Waters Corp. liquid chromatograph [refractive index detection, Millenium GPC V software,
- 20 Phenogel-10, 7.8x250 mm column: 10-4A, 500A & 50A, THF eluent]): Mw=23, 800; Polydispersity 2.76.

Formulation Examples

Example 8: Formulation of 30% t-Butyl derivatized poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate)

For 35 g of imaging layer solution (total 9 weight % solids),
5 2.92 g of 30% t-butyl ester blocked poly(monomethyl maleic acid-allyltrimethylsilane-t-butyl-methacrylate) of Example 3 and 0.230 g of a triarylsulfonium perfluorooctan sulfonate photoacid generator were combined and dissolved in 31.85 g of propylene glycol methyl ether acetate (PGMEA). The mixture was rolled until the components dissolved, and the
10 imaging layer solution was filtered twice through a 0.1 μm Teflon filter.

Example 9: Formulation of 38% t-Butyl derivatized poly(monomethyl maleic acid-allyltrimethylsilane-t-butylmethacrylate)

For 35 g of imaging layer solution (total 9 weight % solids),
15 2.92 g of 30% t-butyl ester blocked poly(monomethyl maleic acid-allyltrimethylsilane-t-butyl-methacrylate) of Example 6 and 0.230 g of a triarylsulfonium perfluorooctan sulfonate photoacid generator were combined and dissolved in 31.85 g of propylene glycol methyl ether acetate (PGMEA). The mixture was rolled until the components dissolved, and the
20 imaging layer solution was filtered twice through a 0.1 μm Teflon filter.

Example 10: Preparation of Bilayer Resist Films

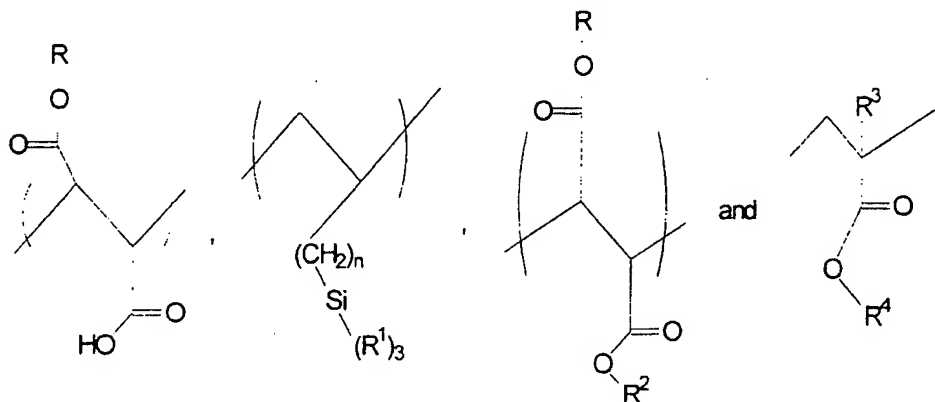
Silicon wafers were spin coated with a thermally curable undercoat and post apply baked at 200°C for 90 sec giving a 5000 Å film
25 thickness. The undercoat was a hexamethoxymelamine thermally cured copolymer of isobornyl methacrylate and hydroxystyrene. The above imaging layer formulations of Examples 8 and 9 were each spin coated over the undercoat of a wafer and post apply baked at 150°C for 60 sec giving a 2500 Å film thickness. The coated wafers were then exposed
30 using an ISI 9300 Microstepper. The wafers were post exposure baked at 150°C for 60 sec and developed for 16 sec in 0.262 N-tetramethyl ammonium hydroxide. The wafers were spun dry and the images were analyzed by scanning electron microscope. The imaging layers using

either Example 8 or 9 were able to resolve 0.13 μm dense features at a 1:1 pitch.

With the foregoing description of the invention, those skilled in the art will appreciate that modifications may be made to the invention without departing from the spirit thereof. Therefore, it is not intended that
5 the scope of the invention be limited to the specific embodiments illustrated and described.

We Claim:

1. A radiation-sensitive derivatized copolymer comprising structural units of the formulae:



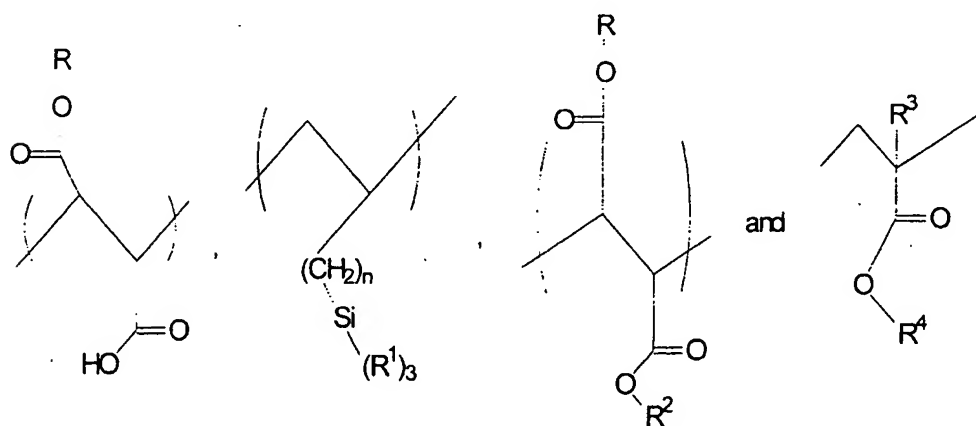
5

wherein n is an integer of from 1 to 5, R is the alkyl radical, R^1 is methyl or trimethylsiloxy, R^3 is hydrogen or methyl and R^2 and R^4 are t-butyl radicals.

2. A radiation-sensitive derivatized copolymer of Claim 1 wherein n is 1, R is CH_3 , R^1 is methyl and R^3 is hydrogen.
3. A radiation-sensitive derivatized copolymer of Claim 1 wherein the level of t-butyl derivatized carboxylic acid groups is from about 20 to about 53% of the carboxylic acid groups.
4. A radiation-sensitive derivatized copolymer of Claim 2 wherein the level of t-butyl derivatized carboxylic acid groups is from about 20 to about 53% of the carboxylic acid groups.

20

5. A radiation-sensitive derivatized copolymer of Claim 1 wherein the derivatized copolymer has a molecular weight (Mw) of from about 10,000 to about 40,000 and a silicon content of from about 8 to about 12% by weight.
- 5
6. A radiation-sensitive derivatized copolymer of Claim 4 wherein the derivatized copolymer has a molecular weight (Mw) of from about 10,000 to about 40,000 and a silicon content of from about 8 to about 12% by weight.
- 10
7. A radiation-sensitive derivatized copolymer according to Claim 1 comprising a derivatized copolymer having from about 40 to about 50 mole % maleic anhydride units, about 40 to about 50 mole % allyltrimethylsilane units and up to about 20 mole % t-butylacrylate units.
- 15
8. A radiation-sensitive photoresist composition comprising:
a derivatized copolymer comprising structural units of the formulae:



20

wherein n is an integer of 1 to 5, R is the alkyl residue of alkanol, R¹ is methyl or trimethylsiloxy, R³ is hydrogen or methyl and

R^2 and R^4 are tert-butyl radicals,

a photosensitive compound which generates an acid upon exposure to actinic radiation, and

5

a solvent capable of dissolving the derivatized copolymer and the photosensitive acid generating compound.

9. A radiation-sensitive photoresist composition according to Claim 8
10 wherein R is CH_3 , R^1 is methyl and R^3 is hydrogen.
10. A radiation-sensitive photoresist composition according to Claim 8
15 wherein the level of t-butyl derivatized carboxylic acid groups in the derivatized copolymer is from about 20 to about 53% of the carboxylic acid groups.
11. A radiation-sensitive photoresist composition according to Claim 9
20 wherein the level of t-butyl derivatized carboxylic acid groups in the derivatized copolymer is from about 20 to about 53% of the carboxylic acid groups.
12. A radiation-sensitive photoresist composition according to Claim 8
25 wherein the derivatized copolymer has a molecular weight (Mw) of from about 10,000 to about 40,000.
13. A radiation-sensitive photoresist composition according to Claim 11
wherein the derivatized copolymer has a molecular weight (Mw) of from about 10,000 to about 40,000.
- 30 14. A radiation-sensitive photoresist composition according to Claim 8 comprising a derivatized copolymer having from about 40 to about 50 mole % maleic anhydride units, about 40 to about 50 mole % allyltrimethylsilane units and up to about 20 mole % t-butylacrylate

units.

15. A radiation-sensitive photoresist composition according to Claim 8
wherein the photosensitive acid generating compound is a
5 triarylsulfonium perfluoro sulfonate compound.
16. A process for forming a pattern on a substrate which comprises:
- (a) coating a photoresist coating of the radiation-sensitive
photoresist composition of Claim 8 over a planarizing
10 undercoat on a wafer substrate;
- (b) exposing portions of the photoresist coating to actinic
radiation; and
- (c) developing the photoresist coating with a developer solution
to provide a patterned substrate.
- 15
17. The process according to Claim 16 wherein the actinic radiation has
a wavelength of about 193 nm.
18. The process according to Claim 17 wherein the planarizing
20 undercoat on the wafer substrate is a coating of a melamine cured
copolymer of isobornyl methacrylate and hydroxystyrene.
19. A process for the lithographic treatment of a substrate comprising:
- 25 (a) providing an undercoat of a film-forming aromatic polymer on
the substrate;
- (b) providing over the undercoat a second coating containing a
derivatized copolymer according to Claim 1 and a photoacid
generating compound that generates acid under the effect of
30 actinic radiation of a wavelength of about 193 nm;
- (c) irradiating the thus coated substrate of step (b) in an image-
forming manner with radiation of a wavelength of about 193
nm;

- (d) subjecting the irradiated substrate to heat;
 - (e) treating the irradiated substrate with an aqueous-alkaline developer solution until the irradiated regions of the second coating are removed; and
 - 5 (f) treating the coated substrate of step (e) with an oxygen-containing plasma until the undercoat is completely removed on those places where it is not covered by the second coating.
- 10 20. A patterned substrate produced according to the process of Claim 16.